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(54) Electrochemical gas sensor

(57) An electrochemical gas sensor 3 for detecting concentrations of gases comprises a hollow body 13 defining an open chamber for containing electrolyte, a cap 11 covering an opening to the chamber, and a membrane 25 fitting between the cap and the chamber. The cap is formed with a passage 14 to allow gas to enter the cell. The membrane 25 is permeable to the gas to be detected but impervious to the electrolyte, and carries a catalytic electrode 36 on its face adjacent the chamber. A collector wire 23 is positioned against the electrode to make electrical contact with the electrode. The membrane is welded near its outer edge, to the body, the weld forming a seal between the membrane and the body, and securing the wire in position. The cap 11 has a projection 18 bearing against the outer face of the membrane to hold the membrane and the collector wire against one another. The cap 11 is secured to the body 13 by welding.

A wick conducts electrolyte to a pad 38 adjacent the working electrode 36 and one or two further electrodes are provided in the body 13, as shown on a further membrane 30 located behind a further cap 12.

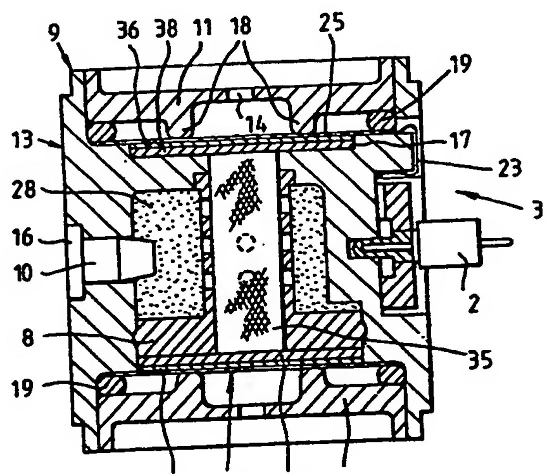

FIG. 1

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

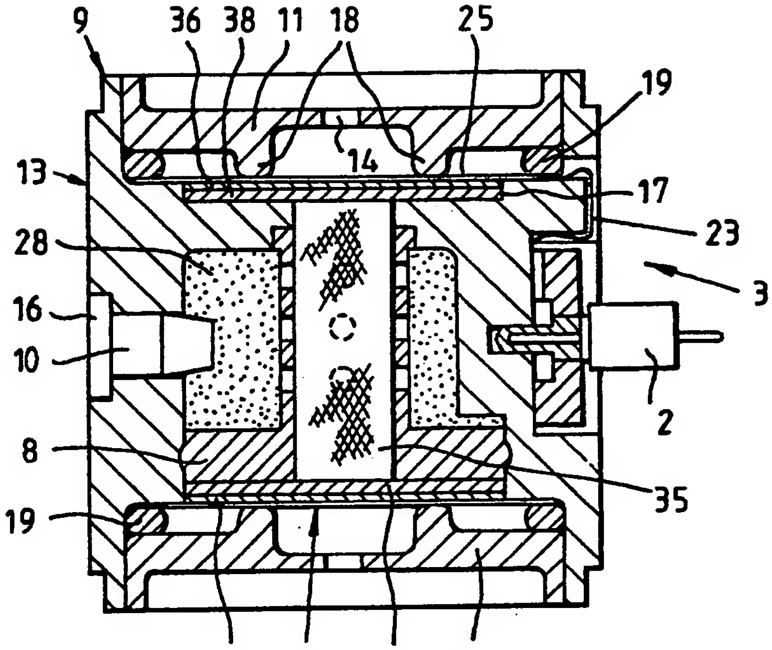
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FIG. 1

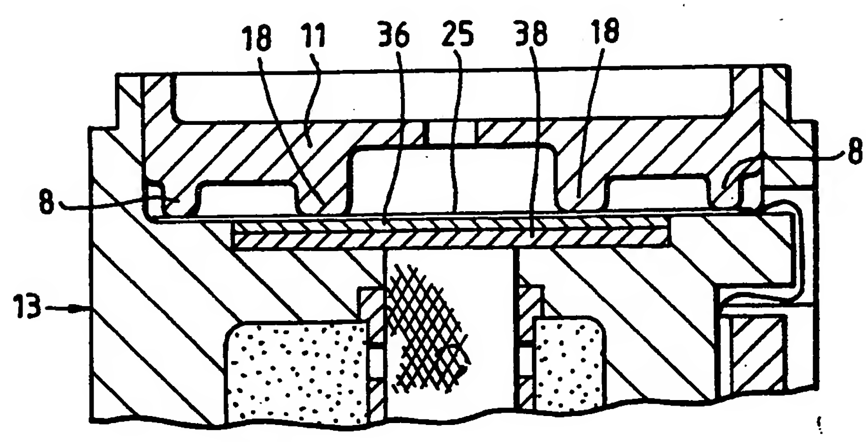
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FIG. 4

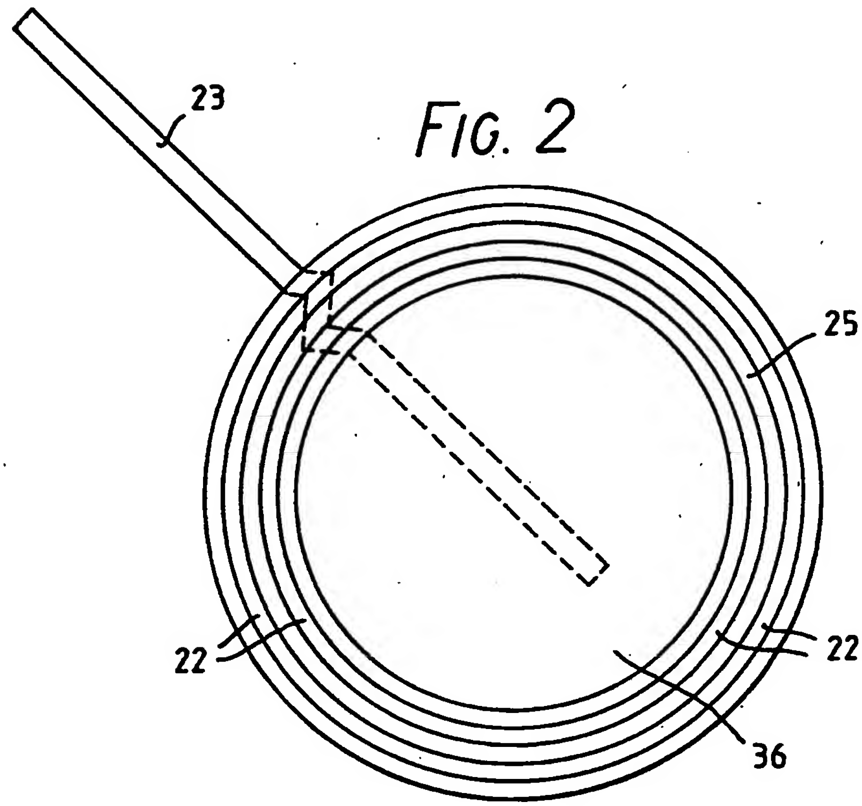

FIG. 2

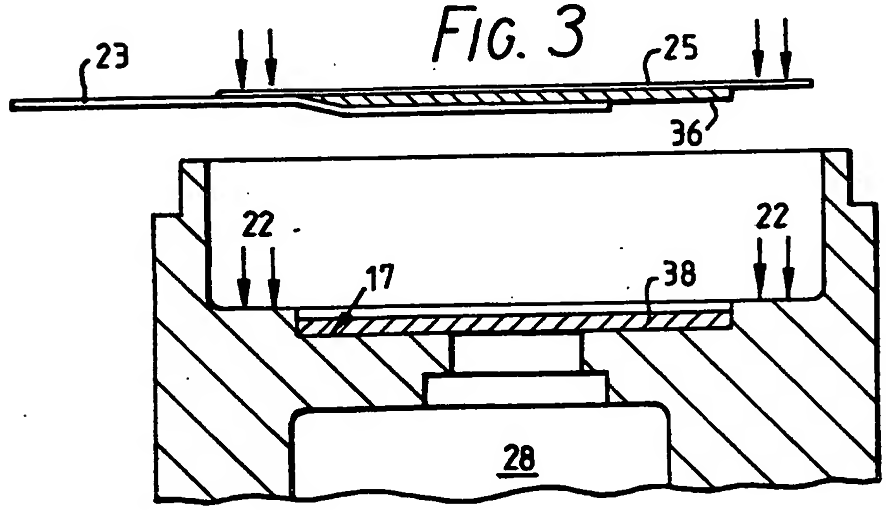

FIG. 3

ELECTROCHEMICAL GAS SENSOR

The present invention relates to a sensing technique using electrochemical means for monitoring the presence or concentration of gases or vapours in the atmosphere.

Many of the sensors currently used to detect gases and vapours make use of a fuel cell principle whereby a current is generated as a result of electrochemical oxidation or reduction of the species being detected on a catalytic electrode. This current generation or amperometric technique is used as a measure of the gas concentration.

Electrochemical cells such as that described in this invention comprise either two or three electrodes separated in space but in contact with an electrolyte. The working or sensing electrode is in contact with the atmosphere being monitored. A condition of the operation of the working electrode must be such that contact between the gas, the electrode catalyst and the electrolyte is achieved. One commonly used cell construction includes a gas diffusive membrane onto which the catalyst is deposited or coated which allows passage of the gas to the catalyst but prevents egress of the electrolyte from the cell. A counter electrode similar to the working electrode is provided to complete the circuit in the cell. A reference electrode may also be provided to establish, with the aid of electronic circuitry, a fixed potential relative to which the working electrode can be biased.

Means are provided for taking the current generated between the counter and working electrodes to an exterior circuit for measurement. These means usually comprise metal collector strips that contact the electrodes and connect to the exterior circuit.

The three electrodes are connected by using a circuit containing a potentiostat that holds the reference electrode to a fixed

potential. Under most circumstances, the working electrode is held to a potential that is fixed relative to the reference electrode. Measurement of the current generated as a result of exposure of the working electrode to the gas may then be made. The magnitude of the current is related to the concentration of the gas by a relationship such as:

$$\text{Current,} \quad I = nFA\,(C1 - C2)\,/\,e$$

where:

n = number of electrons generated per molecule of gas reacting,

F = Faraday's number

A = area of electrode

$C1 - C2$ = concentration difference across diffusion envelope, that is, the difference in concentration between the region where the gas is most concentrated (ie. the atmosphere being tested) and the region where it is least concentrated (ie. adjacent the working electrode),

e = length of diffusion path, that is the distance between the ambient atmosphere and the working electrode.

Under normal circumstances, a restriction of the gas flow to the electrode is provided so that the rate-limiting step in the above equation is that of mass transport of the gas to the electrode surface. In such a case, the concentration of gas at the electrode may be taken to be essentially zero, as reaction at the surface is rapid, and the current I is directly proportional to the concentration of the gas outside the cell. This is borne out in practice with a linear relationship, provided that the gas is present at below saturation concentrations.

Sensors used for monitoring toxic gases have a requirement of reliability and lack of susceptibility to false alarm over a range of environmental conditions. In order to ensure that a false indication of a hazard is not provided when toxic gas is not present, sensors are developed that are specific to the particular

toxic gas to be detected, and which have a minimal response to gases that are not a hazard. In addition, it is ensured that the influence of environmental effects such as changes in humidity or temperature on the performance of the cell are minimised during the design stage so that the indication of a hazard from the instrument using the electrochemical cell is due to the presence of the toxic gas and not as a result of changes in the environment.

However, there are two potential causes of failure of electrochemical cells of this type: either leakage of electrolyte from inside the cell to the outside which may attack the connector terminals or may deplete the electrolyte volume to a level that is insufficient for the cell to operate; or poor electrical contact between the current collector and the working catalytic electrode.

These problems may be traced to the method of construction of the cell. A common method used to hold the cell together involves the use of nuts and bolts which hold the membranes in place and provide a seal using O-rings. The current collectors are held against the electrode by pressure against an absorbant pad. The disadvantage of such a method lies in the reliance on the O-ring to return a steady pressure during the life of the cell. This is not always the case and the electrolyte may leak between the membrane and the cell body as the O-ring becomes less effective with age. If the connector does not form a reliable contact with the elctrode, the reading from the cell will be inaccurate. Misleading indications of concentrations of toxic gases are, of course, extremely dangerous in the human environment.

According to the present invention there is provided an electrochemical cell for detecting concentrations of gases, the cell comprising a hollow body defining an open chamber for containing electrolyte, a cap for covering an opening to the chamber, the cap being formed with a passage for allowing gas to enter the cell, and a membrane fitting between the chamber and the cap, the membrane being permeable to the gas to be detected but impervious to the electrolyte, and the membrane carrying an electrode on its face

adjacent the chamber, the cap being sealed to the body, and the membrane being secured by welding to the body or the cap. With such an arrangement, the electrolyte cannot leak from the welded seal. Preferably, the seal between the cap and the body is also effected by welding.

In a preferred form of the invention, the periphery of the membrane is welded to the body, and a collector wire is provided for making an electrical contact to the elctrode, the collector wire being positioned against the membrane to make electrical contact with the electrode, and being secured in position by the welding between the membrane and the body. By securing the wire in the welded joint between the body and the membrane, the wire cannot easily come away from the membrane. This makes the cell more durable in use.

Preferably, the cap is formed with a projection for bearing against the face of the membrane to retain the electrode in electrical contact with the collector wire.

Embodiments of the invention will now be described with reference to the accompanying drawings, of which:

Figure 1 is a sectional view from the side of an electrochemical gas sensing cell;

Figure 2 is a view from above showing the membrane of the cell in figure 1 on an enlarged scale;

Figure 3 is a sectional view showing the construction of the cell of figure 1; and

Figure 4 is a sectional view through a portion of an alternative construction of the cell.

Referring to figure 1, an electrochemical gas-sensing cell 3 includes a hollow cylindrical body 13, made of a polymeric plastics material that is resistant to strong acids and gases. Suitable

materials are ,for example, polypropylene, polytetrafluoroethylene and polyethlene. The hollow body 13 defines a chamber 28 for containing liquid electrolyte essential in the electrochemical process.

The chamber 28 is open at its opposite ends. The electrolyte is retained in the cell 3 by membranes 25,30 fitting across the open ends. The membrane 25 carries a working electrode 36 on its face adjacent the chamber, and the membrane 30 carries a split electrode 37. Each electrode is constructed from a precious metal/PTFE mix, and is bonded to a porous fluoropolymer sheet membrane. This membrane is hydrophobic and, as such is not 'wetted' by the electrolyte, thus the membrane is impervious to the electrolyte, thereby preventing its escape from the cell. On the other hand, the membrane is permeable to the gas to be detected, allowing the gas to flow into the cell and to react on the working electrode 36.

Each membrane 25, 30 is in the form of a circularly shaped porous sheet. The membrane typically has a porosity of between 10% and 20%, and a thickness of between 0.003 and 0.009 inches.

The working electrode 36 is prepared by mixing a catalyst and PTFE suspension in water to form a pliable cohesive mass. The catalyst is typically a precious metal in powder form, such as platinum, palladium, iridium, or gold. The mixture is applied to the membrane using techniques well known to those versed in the art. Typically, the mixture is formed into a thin film, applied to the membrane, and heated to a temperature of say 200°C to fuse it to the membrane. The catalyst electrode covers a circular area of the membrane, the periphery of the membrane being left uncovered.

The split electrode 37 comprises two separate portions forming a reference electrode and a counter electrode.

The counter terminal is itself a catalytic electrode, as it takes part in a catalytic reaction with ions introduced into the electrolyte by the working electrode. The catalyst for the counter

electrode may be different from that on the working electrode.

For example, say that a toxic gas hydrogen sulphide (H_2S) is being detected at the working electrode. The chemical reaction at the working electrode would be:

$$H_2 + 4H_4O \qquad H_2SO_4 + 8H^+ + 8e^-$$

The H^+ ions introduced into the electrolyte at the working electrode migrate to the counter electrode where they undergo a catalytic reduction to gain electrons from the counter electrode.

The reference electrode is also a catalytic electrode, although it does not itself take part in a chemical reaction. Catalytic material is used for the reference electrode for convenience, so that the reference electrode may be formed in the same manufacturing process as the counter electrode. The split electrode 37 may be constructed in a similar fashion to the working electrode, the catalyst being arranged on the membrane 30 as two separate portions for the counter and reference electrodes.

The membranes 25,30 are sealed to the body 13 by welding. Suitable methods of welding are heat welding and ultrasonic welding.

A first cap 11 fits over the working electrode 25. The cap is sealed to the body by welding. Suitable methods of welding are ultrasonics welding, and heat welding. The cap is formed with a passage 14 to allow gas outside the cell to enter the cell.

A second cap 12 fits over the membrane 30, in a similar manner to the fitting of the first cap 11. The second cap 12 is sealed to the body 13 by welding. A hole 15 is provided in the second cap to equilibriate pressure changes occuring at the working end of the cell 13.

The chamber 28 contains a reservoir of electrolyte, and a wick holder 8. The wick holder 8 is filled with absorbent material that

acts as a wick to draw liquid electrolyte from the reservoir and deliver it to the working electrode 36. An absorbant pad 38 of glass fibre lies against the face of the electrode 36 and assists in bringing the electrolyte into contact with the electrode. Thus the wick and the absorbant pad ensure that the electrolyte remains in contact with the precious metal electrode regardless of the orientation of the cell 13. A hole 16 is provided in the wall of the body to allow the reservoir to be filled with electrolyte. A plug 10 is welded into the hole 16 once the cell 13 has been filled.

The current generated electrochemically at the elctrodes 36,37 is transmitted from the electrodes by means of platinum collector wires 23,24 touching the electrodes 36,37 respectively. The wires 23,24 are connected to a plastics terminal connector 2 formed on the outside of the body 13. The connector houses a terminal for each electrode, or electrode portion, and is designed to receive a plug (not shown) to connect the cell to monitoring circuitry (not shown).

The constructional details of the electrode 36, the collector wire 23 and the membrane 25 may be more clearly understood by referring to figures 2 and 3.

The edge of the opening to the chamber is formed with an annular recess 17 having a depth equal to the combined thickness of the electrode 36 and the absorbant pad 38. The electrode 36 extends across the opening to the chamber, and has its edge locating in the recess 17. The periphery of the membrane extending beyond the electrode rests against the edge of the opening beyond the recess. The collecting wire 23 is positioned flat against the electrode to extend substantially radially between the electrode and the absorbant pad and is held in place by pressure between the electrode and the absorbant pad, thereby providing touch contact between the electrode 36 and the collecting wire 23.

The membrane is sealed to the body by welding of the periphery of the membrane to the upper portion of the opening to the chamber. The welding is effected in two concentric bands, as shown by the

circles 22 in figure 2. The collector wire is thus secured in position by the welding joint around the wire. During the welding process the plastics materials of the membrane and body soften and flow around the wire to form a good seal. The collecting wire may follow a zig-zag pattern on the periphery of the membrane where the membrane is attached to improve the seal around the wire.

The cap 11 is formed with an annular projection 18 which, when the cap is fitted, bears against the outer face of the membrane to retain the electrode in touch contact with the collector wire. An O-ring seal 19 is provided as a further seal between the membrane and the cap. The O-ring is compressed only slightly as it does not have to provide a strong force to press the collector wire and the membrane against one another, nor does it have to effect a seal between the membrane 25 and the body 13. Since the cap does not have to be welded in position while under pressure to compress the O-ring 19, the fitting of the cap is simpler and its positioning less critical.

The membrane 30, the wires 24 and the second cap 12 may be fitted to the opposite end of the cell in a similar manner to that described above.

An alternative embodiment of the cell is shown in figure 4. In this embodiment, the O-ring has been replaced by a second annular projection 8 formed on the cap 11. The second annular projection 8 acts as a spacer to locate the cap 11 in the correct position in the opening for welding.

In the embodiments described above a hermetic seal is formed between the membrane, the collector wire and the body ensuring that electrolyte will not leak out from the cell at these seals. This hermetic seal will not deteriorate with time. Furthermore, the seals trap the collector wires in position in good electrical contact with the electrodes. Thus the problems of leakage and of poor electrical contact, which occur with age in some conventional designs, are avoided.

In the embodiments described above, the elecrolyte is delivered to the working electrode by means of the wick and the absorbant pad. This ensures that there is always a plentiful supply of electrolyte at the electrode, regardless of the orientation of the cell while in use. The reservoir is filled with electrolyte to prevent drying out under most conditions.

In the embodiments described above, the cell has a terminal connector for connecting to external monitoring circuitry. This enables the cell to be easily 'plugged-in' to the circuitry, while at the same time ensuring that a reliable connection is made.

It will be appreciated that in the embodiments described, the designs of the body and of the caps are such that these components may be readily moulded from suitable plastics material.

Although in the embodiments described, the membrane is welded to the body, in other embodiments the membrane may be welded instead to the cap. In this case, it is preferred that the cap be secured to the body by welding so that a reliable and durable seal is obtained to prevent leakage of the electrolyte.

Although in the embodiments described, the opposite electrode to the working electrode is a split electrode with portions forming a reference electrode and a counter electrode, in other embodiments the reference electrode may be omitted. The electrode would then be formed as a single electrode.

CLAIMS

1. An electrochemical cell for detecting concentrations of gases, the cell comprising a hollow body defining an open chamber for containing electrolyte, a cap for covering an opening to the chamber, the cap being formed with a passage for allowing gas to enter the cell, and a membrane fitting between the chamber and the cap, the membrane being permeable to the gas to be detected but impervious to the electrolyte, and the membrane carrying an electrode on its face adjacent the chamber, the cap being sealed to the body, and the membrane being secured by welding to the body or the cap.

2. A cell according to claim 1, wherein the cap is sealed to the body by welding.

3. A cell according to claim 1 or 2, wherein the periphery of the membrane is welded to the body, further comprising a collector wire for making an electrical connection to the electrode, the collector wire being positioned against the membrane to make electrical contact with the electrode, and being secured in position by the welding between the membrane and the body.

4. A cell according to claim 3, wherein the collector wire follows a zig-zag pattern in the region of the weld at the periphery of the membrane.

5. A cell according to claim 3 or 4, wherein the membrane is circularly shaped, and the welding is effected in two concentric bands near the edge of the membrane.

6. A cell according to claim 3,4 or 5, wherein the periphery of the membrane extends beyond the edge of the electrode, and the edge of the opening to the chamber is formed with a recess, the electrode extending across the opening and having its edge located in the recess, the collector wire being trapped against the edge of the

electode in the recess.

7. A cell according to claim 6, wherein an absorbant pad fits adjacent the face of the electrode adjacent the chamber, the absorbant pad covering substantially the face of the electrode and having its edge located in the recess with the edge of the electrode, the recess having a depth equal to the combined thickness of the electrode and the pad, the collector wire being trapped between the electrode and the absorbant pad.

8. A cell according to any of claims 3 to 7, wherein the cap is formed with a projection for bearing against the outer face of the membrane to retain the electrode in position in contact with the collector wire.

9. A cell according to any of the preceding claims, wherein the welding is achieved by a process of heat welding.

10. A cell according to any of the preceding claims, wherein the welding is achieved by a process of ultrasonic welding.

11. A cell according to any of the preceding claims, wherein the chamber contains a reservoir for holding electrolyte, and a wick for delivering electrolyte to the electrode.

12. A cell according to any of the preceding claims, wherein the electrode comprises a catalyst applied to the membrane.

13. A cell according to claim 12, wherein the catalyst is a precious metal.

14. A cell according to any of the preceding claims, wherein the membrane is made of porous PTFE material.

15. A cell according to any of the preceding claims, wherein the body has a second opening at the opposite end to the first-mentioned opening, further comprising a second cap for covering the second

opening, the cap being formed with a hole to allow for equilibration of internal and external gas pressures of the cell, and a second membrane fitting between the chamber and the second cap, the second membrane being permeable to the gas to be detected but impervious to the electrolyte, and the second membrane carrying a second electrode on its face adjacent the chamber, the second cap being sealed to the body, and the second membrane being welded to the body or the second cap.

16. A cell according to claim 15, wherein the second electrode is a split electrode comprising two separate electrode portions.

17. A cell according to any of the preceding claims, further comprising an electrical connector for connecting the cell to external monitoring circuitry, the connector including a terminal for each electrode or electrode portion, and being connected to the electrodes by collector wires.

18. A cell substantially as hereinbefore described with reference to figures 1 to 3 of the accompanying drawings.

19. A cell substantially as hereinbefore described with reference to figure 4 of the accompanying drawings.

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